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Specification

1. Name of the Invention

Secondary battery

2. Claim

A secondary battery characterized by a conductive polymer molded into a cylinder.

3. Detailed Description of the Invention

[Industrial Field of Application]

The invention relates to a secondary battery utilizing a conductive polymer.

[Prior Art]

Secondary batteries using a mixture electrode made of conductive polymer were proposed in Publication of unexamined patent application numbers 62-243248, 62-193061, 62-176068, 62-93865, and 62-168348.

One of the typical mixture electrodes made of conductive polymer is a pellet type, which is manufactured by compressing and molding a mixture of a conductive high polymer, a binder such as polytetrafluoroethylene, and a conductive agent such as carbon black, and is especially suitable for small capacity batteries such as button cell. When this mixture electrode is used for a large capacity battery to supply high current, the above mixture is coated onto a collector such as metal mesh, compressed and molded into a mixture electrode sheet integrating the collector, and coiled into a spiral together with a separator and an opposing electrode.

However, when coiled into a spiral, the mixture electrode is likely to crack, peel, and twist, and is not suitable for practical application. To solve this problem, Publication of unexamined patent application number 62-93865 proposes that an aniline polymer and fluororesin be dispersed in water and that a water soluble organic compound with low boiling point be added; this method, however, does not fully correct the problem. Presently, none of the existing electrodes is satisfactory as a large capacity cell to produce high current.

[Problems Intended to be Solved by the Invention]

The invention intends to offer a secondary battery with a new design that prevents cracking, peeling, and twisting of a mixture processed into a sheet plate and coiled into a spiral, while maintaining the advantages of a spiral electrode including its extensive contact with an electrolyte and a wide area between its opposing electrode.

[Means of Solving Problems]

The inventors, while studying to solve the problems above, discovered that molding a conductive polymer into a cylindrical electrode is effective, and conceived the invention.

The invention is therefore a secondary battery characterized by its cylindrical electrode molded from a conductive polymer. The electrode, while most desirably cylindrical, may be a polygonal pole with 3, 4, or 6 faces as needed.

The cylindrical mixture electrode according to the invention is in contact with an electrolyte at two surfaces, external and internal; likewise the electrode faces its opposing electrode at these two surfaces. If needed, cylindrical electrodes of different sizes may be positioned concentrically, and a separator and an opposing electrode may be positioned in between the electrodes; this virtually equals to a spiral electrode without the problem of cracking, peeling, and twisting that the mixture electrode sheet is subjected to when it is coiled.

With reference to collecting current, an example would be a collector shaped like a comb; each of its teeth is connected to a cylindrical electrode to collect current from all cylindrical electrodes.

Conductive polymers used in the invention are, for example, polypyrrole, polythiophene, polythiazyl, polyacetylene, polyparaphenylene, polyparaphenylene sulfide, polyaniline, polyparaphynylene vinylene, polyisothianaphthene, polypyridazine, polyazulene, polyselenophene, polypyridine, polyacene, and poly-perinaphthalene.

Dopants for these conductive polymers include BF_4-, ClO_4-, PF_6-, AsF_5, SbF_5, Na, I_2, K, and Br_2.

Resin binders used in the invention may be a fluororesin such as polytetrafluoroethylene and vinylidene fluoride, or a polyalkylene resin such as ethylene – vinyl acetate copolymer, ethylene – ethylacrylate copolymer, epoxy resin, polyvinylalcohol, polyester resin, polyethylene, and polypropylene. An appropriate resin binder is selected out of these depending on the

conductive polymer, conductive agent, and electrolyte used; a resin that, with only a small amount used, binds conductive polymers and agents effectively without dissolving or expanding into an electrolyte should be selected. However, these resin binders are not necessarily required; some of the conductive polymers (for example polyaniline) are compressed and molded into a cylindrical electrode according to the invention without a binder. In such cases, it is desirable not to use a resin binder to increase the ratio of a conductive polymer per unit volume of the positive electrode.

While conductive agents may be a carbon material such as Ketchen [transliterated] black, acetylene black, and graphite, and micro metal particles or metal staple fiber such as SUS staple fiber, platinum, gold, and silver, carbon materials are more desirable.

Next, the method to manufacture a cylindrical mixture electrode according to the invention using these conductive polymers, conductive agents, and resin binders will be described below.

A conductive polymer (powder is desirable), a conductive agent, and a resin binder (powder, solution, or dispersion) are mixed, and the mixture is compressed in a cylindrical mixture mold and vacuum-dried (vacuum-drying is not needed if the resin binder is powder).

The weight ratio of the conductive polymer, conductive agent, and resin binder is 60 to 100 weight % or more desirably 80 to 95 weight % of the conductive polymer, 0 to 40 weight % or more desirably 5 to 20 weight % of the conductive agent, and 0 to 20 weight % or more desirably 0 to 10 weight % of the resin binder.

While the conductive polymers used in the invention may be produced by electrolytic or chemical polymerization, those chemically polymerized are more desirable because they are in the powder form that is convenient for mixing, and because they are produced in large volumes.

When a cylindrical mixture electrode according to the invention is used as a positive electrode in a secondary battery, zinc, aluminum, magnesium, lithium, and cadmium as well as semiconductive polymers dissimilar to the positive electrode may be used as a negative electrode.

When a cylindrical mixture electrode according to the invention is used as a negative electrode in a secondary battery, manganese dioxide, silver oxide, fluoro graphite, thionyl chloride, activated carbon, titanium disulfide, and molybdenum disulfide as well as semiconductive polymers dissimilar to the negative electrode may be used as a positive

electrode. Naturally, both positive and negative electrodes may be a cylindrical mixture electrode according to the invention made of conductive polymer.

As an electrolyte, an aqueous solution of metal halide or a solution of organic solvent may be used. When the negative electrode is lithium, an electrolyte should be an organic solvent; for example it is selected from γ-butyrolactone, propylene carbonate, dimethylformamide, and dimethoxyethane. As a supporting electrolyte, ammonium chloride is used for aqueous solutions and lithium perchlorate and lithium borofluoride are used for organic solvents.

[Working Examples]

The invention will be further detailed with reference to its working examples.

Working Example 1

(1) Synthesizing chemically polymerized polyaniline

20.4 g (0.219 mol) of aniline was dissolved in 300 ml of an aqueous 1MHCl solution, 11.5 g (0.0504 mol) of $(NH_4)_2S_2O_8$ was dissolved in 200 ml of an aqueous 1MHCl solution, and the second solution was instilled into the first solution and mixed while the temperature was kept at 5 to 10°C below zero. When the instillation process was completed, the mixture was continuously stirred for 2 hours at the same temperature, and the precipitating aniline (powder) was filtered. Polyaniline thus obtained was washed in 200 ml water 3 times and 100 ml of methanol twice then dried.

The resulting polyaniline was stirred in 300 ml of a 20% methanol solution of hydrazine for 2 hours at room temperature, de-doped, reduced, and filtered. The resulting polyaniline was again stirred in 300 ml of a 20% methanol solution of hydrazine. This de-doping/reduction process was repeated 5 times, and the filtered product was washed in 100 ml of methanol twice to obtain 10.0 g of light blue polyaniline.

(2) Creating cylindrical mixture electrode

1.56 g of the polyaniline above and 0.16 g of graphite (KS-6 by Ronza) were thoroughly mixed and compressed in a mold at a pressure of 100 kg/cm^2, resulting in a cylindrical electrode 40 mm high with an OD of 9.5 mm and an ID of 6 mm shown in Figure 1.

(3) Evaluation of the battery performance

A cell for evaluation shown in Figure 2 was created using the cylindrical electrode above as a positive electrode, a lithium sheet (50 μm thick by Honjo Metals), a separator (Juraguard by Polyplastics), and an electrolyte that is a 3M solution of 70 vol% of propylene carbonate of $LiBF_4$ and 30 vol% of dimethoxyethane; and the cell was tested for charge/discharge performance.

The evaluation method was as follows.

A charge/discharge test was conducted with the final charge voltage set to 3.8 V, the final discharge voltage to 2.3 V, and the charge/discharge current to 20 mA. The energy density of the positive electrode was 348 Wh/kg. The positive electrode retained its shape with no cracking or peeling after 100 times of charge/discharge operation.

Working Example 2

2 g of polyaniline, 0.2 g of Ketchen black (Ketchen Black EC by Lion), 0.33 g of Teflon dispersion (D-2 by Daikin, 60 wt% solid), and 2.27 g of water were mixed well; 3.44 g of this mixture was compressed in a mold at a pressure of 100 kg/cm^2, resulting in a cylindrical electrode 43 mm high with an OD of 9.5 mm and an ID of 6 mm. This cylindrical electrode was dried in vacuum at 100°C for 5 hours.

The dried cylindrical electrode was used as a positive electrode and tested for charge/discharge performance in the same manner as Working Example 1.

The energy density of the positive electrode was 352 Wh/kg, and the positive electrode retained its shape with no changes in appearance after 100 times of charge/discharge operation.

Reference Sample 1

2.81 g of polyaniline and 0.28 g of graphite (KS-6 by Ronza) were mixed well and compressed in a mold at a pressure of 100 kg/cm^2, resulting in a cylindrical electrode 9.5 mm in diameter and 40 mm high. This cylindrical electrode was used as a positive electrode; a separator (Juraguard by Polyplastics) was coiled around the electrode; a lithium sheet (50 μm thick by Honjo Metals) was coiled around the separator; and a resulting cell similar to Working Example 1 was tested for charge/discharge performance.

The energy density of the positive electrode was 23/Wh/kg. The positive electrode registered cracks in the vertical direction after 100 times of charge/discharge operation.

Reference Sample 2

A stainless (SUS 316) expand metal 0.1 mm thick with a mesh size of 2 mm x 1 mm was cut into a segment 100 mm long and 40 mm wide, which was coated with the mixture in Working Example 2 to a thickness of 2 mm and compressed in a mold at a pressure of 100 kg/cm^2, resulting in a mixture electrode sheet. This electrode sheet was dried in vacuum at 100°C for 5 hours; the dried mixture electrode sheet was coiled around a 5 mm rod and examined for cracking and adherence to the expand metal. The electrode suffered cracks during the drying period after coating, and registered severe cracks when coiled. It also peeled from the expand metal.

[Effect]

As demonstrated above, a secondary battery using a cylindrical mixture electrode according to the invention resists cracking and peeling while it is manufactured or used; it is a highly reliable battery featuring sufficient energy capacity, charge/discharge performance, and stability.

4. Brief Description of the Figures

Figure 1 illustrates a cylindrical electrode used for a secondary battery according to the invention; Figure 2 illustrates a cell used for evaluation of the secondary battery according to the invention.

1: Platinum lead wire for positive electrode; 2: Platinum lead wire for negative electrode; 3: Teflon cap; 4: Electrolyte; 5: Lithium sheet (negative electrode); 6: Juraguard (separator); 7: Cylindrical positive electrode; 8: glass jar.

Figure 1

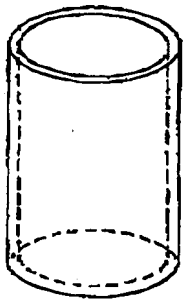

Figure 2